Electronic structure and superconductivity of CaAlSi and SrAlSi

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We report full-potential LAPW calculations for CaAlSi and SrAlSi in ordered structures and in the virtual crystal approximation, at normal and elevated pressures. We also estimate the electron-phonon coupling using either frozen-phon calculations at the zone center, or the rigid muffin tin approximation. We conclude that there is no simple way to explain the recently reported qualitative disparity in the superconducting properties of the two compounds. An assumption of an ultrasoft phonon mode, on the other hand, allows to reconcile in a reasonable way the experimental findings with the theory.

The discovery of superconductivity in MgB_2 called attention to materials with the AlB_2 (C32) layered crystal structure. Some of them, though electronically entirely different from MgB_2, demonstrated interesting superconducting and normal properties. Specifically, CaAlSi and SrAlSi (see Refs.[1-3] and references therein) show superconductivity at $\approx$ 8 and $\approx$ 5 K. Moreover, a closer look reveals a number of interesting and unusual characteristics[1], for instance, a large and opposite in sign pressure coefficient in the two compounds, despite close similarity in the electronic structure. Moreover, thermodynamic measurements suggest that CaAlSi is in a superstrong coupling limit, while SrAlSi is a weakly coupled BCS superconductor.

To understand the physics of these new and interesting systems, we performed accurate band structure calculations, as well as calculations of zone-center phonon modes and their coupling with electrons, and rigid muffin tin estimations of the total electron-phonon coupling constants. While the electron-phonon coupling is sufficiently strong to explain superconductivity at $T_c \lesssim 10$ K, the qualitative difference between the two materials does not find a direct explanation from the electronic or lattice properties.

Electronic structure. X-ray diffraction yields the same hexagonal crystal structure $P6/mmm$ (#191) for both CaAlSi and SrAlSi, with parameters (a, c) equal to (4.189, 4.400 Å) and (4.220, 4.754 Å), respectively[1], which implies that Al and Si are randomly distributed over the $2d$ sites. One may think that upon annealing Al and Si will exhibit some ordering, the simplest models being alternating Al and Si layers with the same symmetry group and twice larger c, or in-plane ordering with symmetry lowering from $P6/mmm$ to $P\bar{6}m2$ (#187), but with the same unit cell. Note that the former ordering is easy to detect by X-rays, while the latter, because Al and Si are neighbors in the Periodic Table, may be easily missed. The latter seems more plausible also from kinetic considerations. As we will show later, it is energetically more favorable in the calculations as well. One can assume that at least some degree of short ordering in plane is always present, therefore we performed most of the calculations in the ordered $P\bar{6}m2$ structure. To estimate disorder effects, we also performed calculations in the average, $P6/mmm$ structure, using the virtual crystal approximation to average over Al and Si.

We used the full potential, all-electron Linear Augmented Plane Wave method in WIEN implementation[4]. A standard setup with the following parameters was used, with the radii of 2.3 bohr for Ca and Sr, and 2 bohr for Al and Si. The cutoff parameter RK_{max} was chosen as 7, which is sufficient because of use of local orbitals and APW's[5]. Gradient correction to the local density approximation was used for the exchange-correlation potential[6]. The resulting bands are shown in Fig. 1. The following observations can be made: (1) Both compounds have very similar bands near the Fermi level; ordering does not change much the band picture either. (2) The bands that play such an important role in MgB_2 are fully occupied here and of no relevance for superconductivity. (3) Only one band crosses the Fermi level. This band is mainly of Ca $d_{3z^2-r^2}-$character, and therefore is quite 3-dimensional. Note that in the virtual crystals an additional small pocket appears near the K point, mainly of Si and Al p_z character. Ordering makes the bonding and the antibonding band at K anticross and this pocket practically disappears in the ordered structure.

Density of states is plotted in Fig.2. Density of states at the Fermi level, $N(E_F)$, is equal to 1.10 st./eV f.u in CaAlSi and 1.33 st./eV f.u in SrAlSi, or, in the virtual crystal approximation, 1.00 and 1.15 st./eV f.u., respectively. The plasma frequencies are $\omega_{p\parallel} = 5.2$ eV, $\omega_{p\perp} = 5.7$ eV for CaAlSi and $\omega_{p\parallel} = 5.7$, $\omega_{p\perp} = 5.9$ for SrAlSi, where $\parallel$ and $\perp$ stand for the in-plane and out of hexagonal plane polarizations. This implies the resistivity anisotropy $\rho_\perp/\rho_\parallel = 1.2$ and 1.03, respectively. The corresponding Fermi velocities are 0.46×10^8 and 0.55×10^8 cm/sec for CaAlSi and 0.48×10^8 and 0.50×10^8 cm/sec for SrAlSi . In other words, the anisotropy is negligible. Interestingly, this is not what the experiments indicate, at least in CaAlSi: the resistivity anisotropy is reported to be 3.1[2], while the coherence length and the penetration length anisotropies, which should in the first approximation follow the Fermi velocity anisotropy, or the square root of the resistivity anisotropy, are of the order of 2[2,3], rather that -10%. This suggests that unusual anisotropic scattering takes place at very low temperatures. or that the conventional bands structure calcula-

tions are exceptionally wrong for these two materials. In either case this would be highly unusual.
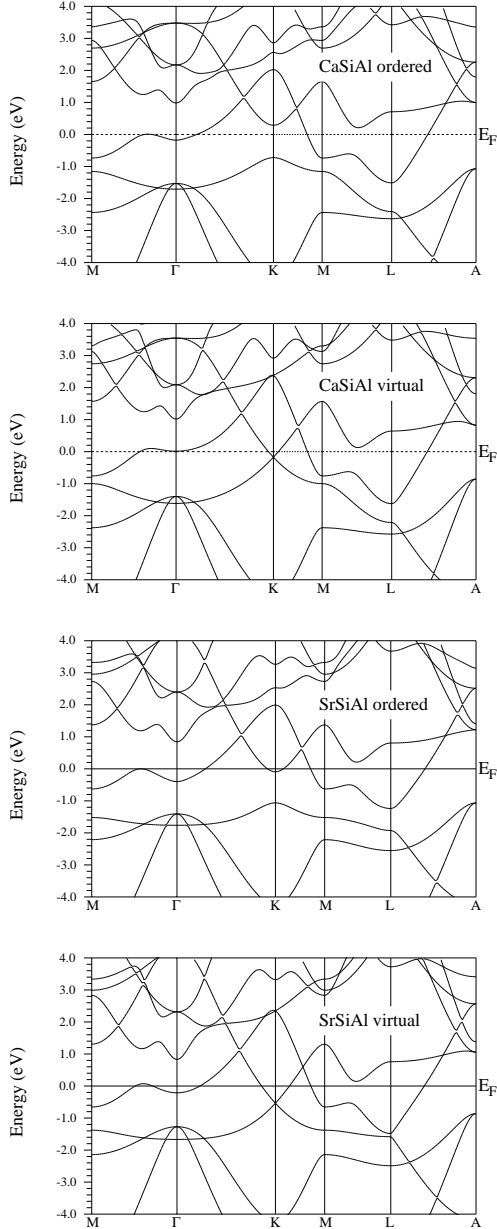

FIG. 1. Band structures of CaSiAl and SrSiAl in the (in-plane) ordered structure and in the virtual crystal approximation.

On the other hand, this discrepancy can be understood if another type of ordering is present at least in CaAlSi: alternating layers of Al and Si. Indeed, this produces a large anisotropy with the right sign ($\omega_{p\parallel}/\omega_{p\perp} \approx 4$), but, as mentioned, kinetic arguments speak against this possibility. However, if such ordering has a substantial energetic advantage, it may occur (and, as one may see, a complete layer-like ordering produces an anisotropy witch is factor of two *too large*). To get more

insight, we performed total energy calculation for both type of ordering. We found, however, that the in-plane ordering is *lower* in energy by 38 mRy (CaAlSi) and 19 mRy (SrAlSi) per formula, a relatively large number (for layered ordering the position of Ca was optimized, but the experimental lattice parameters were used throughout the calculations). Therefore the mystery with the transport anisotropy remains.

Phonons. We used the standard frozen-phonon technique to calculate the frequency of the zone-center phonons and to estimate their coupling with electrons (see, *e.g.*, Ref.[7]). In the P$\bar{6}$m2 structure (in-plane ordering) there are 6 optical phonons, two nondegenerate A_2'' modes (Si and Al displacing along z) and two double-degenerate E' modes (in-plane). Our results are shown in Table I. Interestingly, we found a noticeable anharmonicity for the E' modes in CaSiAl, but not in SrSiAl. As in MgB$_2$ only the phonons of the E symmetry can couple with electrons at the zone center. However, since the σ bands in these compounds never cross the Fermi level, we do not expect large coupling, definitely not on the order of 1, as in MgB$_2$. Because we do not believe that these phonons play a particularly important role here, we did not investigate in details their coupling constants. It sufficed to estimate the coupling constant for the E_{2g} in the virtual crystal approximation, which corresponds to the higher of the two E' modes in the ordered structure.Although we did not force the integration through to the full convergence, we can safely estimate the corresponding λ to be less than 0.05 per each of the two E_g modes, an order of magnitude less than in MgB$_2$.

Getting convinced that all phonons in th entire Brillouin zone couple with the phonons at the same level, we also computed the integral coupling constant in the rigid muffin tin approximation, using a muffin tin APW code, as described in Ref.[8]. We remind the reader that in this approximation the total electron-phonon coupling constant is expressed as

$$\lambda \approx \sum_i \eta_i \Phi_{ii}^{-1}, \tag{1}$$

where the summation is over all atomic species, η is an electronic factor, defined only by the electronic characteristics at the Fermi level, and Φ is the correponding component of the force matrix, a quantity of the order of the atomic mass times an averaged squared phonon frequency[9]. Our results for the electronic factors are given in Table II.

Since we do not know the full dynamic matrix, we take the the force matrices used to compute the frequencies in Table I; Using the E' representation, we obtain for λ in CaSiAl 0.11, with 65% coming from Ca, 10% from Al, and 25% from Si, or, using the A_2'' representation, 0.37, this time, with 15% from Ca, 20% from Al, and 65% from Si. Averaging these results, keeping in mind the degeneracy of the E' representation, we get λ_{RMT}(CaSiAl)$\approx$ 0.20. For SrSiAl the corresponding numbers are $\lambda = 0.16$ (70%:10%:20%) and $\lambda = 0.37$

(20%:20%:60%). The average $\lambda_{RMT}(\text{SrSiAl}) \approx 0.23$. The difference between the two compound is much smaller than the inaccuracy of the rigid muffin tin approximation.
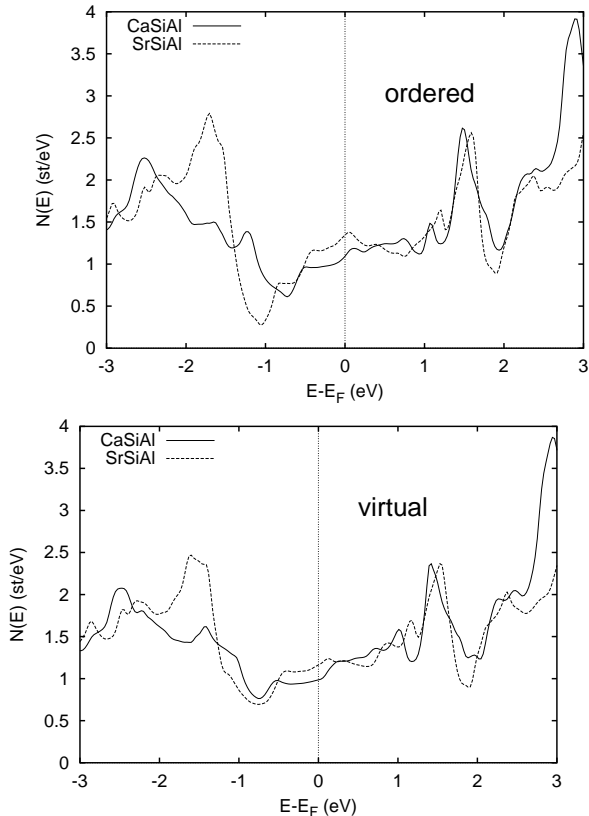

FIG. 2. Densities of states of CaSiAl and SrSiAl in the (in-plane) ordered structure and in the virtual crystal approximation.

It is well known that for the s-p metals this approximation strongly underestimates the electron-phonon coupling; for instance, in MgB_2, one needs to multiply η by three to reach an agreement with the linear response calculations[8]. On the other hand, for d-metals thsi approximations works well[10]. Since these materials appear to have a prominent d-component in their density of states, we may expect that they represent an intermediate case. We can conclude that rigid muffin tin calculations are consistent with the observed superconductivity.

Superconductivity. We shall now try to compose a picture of superconductivity in these compounds as it emerges from the experiment. Probably the most unusual fact about it is that the thermodynamic experiments[1] point to two opposite limits in terms of the coupling strength, and, in a sense, are internally contradictory. Indeed, the measured electronic specific heat coefficients for the two materials are 5.04 and 5.42 mJ/mol K^2. This can be compared to the calculated densities of states, which yield unrenormalized coefficients of 2.59 and 3.13 mJ/mol K^2. Ascribing the difference to the electron-phonon coupling, we find the coupling con-

stant of CaSiAl to be $\lambda = 0.95$, and of SrSiAl to be $\lambda = 0.73$. This agrees with our intuitive expectations that the coupling should be comparable, and also with the fact that the transition temperatures differ by 50-60%. Indeed, for a Coulomb pseudopotential $\mu^* = 0.1$, $\lambda = 0.95$ and $\lambda = 0.73$, the McMillan formula produces, fairly reasonably, a critical temperature difference of 67%, if the average frequency is the same. This, however, places both compounds in a rather strong coupling limit, maybe a bit too strong (with the standard coefficients, $T_c = (\omega_{\ln}/1.2)\exp[-1.04(1+\lambda)/(\lambda - \mu^* - 0.62\lambda\mu^*)]$, the McMillan formula requires the logarithmic frequency of the order of 90 cm^{-1}, unrealistically small). We will get back to these numbers later.

Let us now try to estimate λ entirely from the experiment. For this purpose we can use the numbers for the specific heat jump from Ref.[1], $\delta C_p/\gamma T_c = 2.0$ for CaSiAl and 1.4 for SrSiAl. We shall then make use of semiempirical formulas of Carbotte[11],

$$\frac{\delta C_p}{\gamma T_c} \approx 1.43[1 - 53\alpha^2\ln(3\alpha)], \qquad (2)$$

where $\alpha = T_c/\omega_{\ln}$. Assuming a 5% error bar in the experimental numbers, we get the following limits on α : In CaSiAl $0.061 < \alpha < 0.078$, in SrSiAl . $0 < \alpha < 0.013$. Now we can use the experimental reduced gaps, and another of Carbotte's formulas,

$$\frac{2\Delta}{kT_c} \approx 3.53[1 - 12.5\alpha^2\ln(2\alpha)], \qquad (3)$$

to get another estimate for α (again, assuming 5% error bars): For CaSiAl, $0.061 < \alpha < 0.103$, for SrSiAl, $0 < \alpha < 0.035$. These ranges are compatible with the one obtaind from the specific heat jump, and in fact is larger. Therefore we shall use the first set in the following.

Now we will see what range of λs is this range of αs compatible with. Using the McMillan equation and assuming $\mu^* = 0.12$, we see that $0.061 < \alpha < 0.078$ translates into $0.98 < \lambda < 1.15$, slightly larger, but still in good agreement with our earlier estimate of 0.95, but the condition $\alpha < 0.013$ requires $\lambda < 0.55$, quite below our earlier estimate of 0.73. Furthermore, given the difference in T_c of only 50%, even the lowest estimate for α in CaSiAl, 0.061, when combined with the highest estimate for α in SrSiAl, 0.013, reqires the logarithmic phonon frequency in SrSiAl to be 3 times higher than in CaSiAl, in contradiction with common wisdom, with our calculations for the zone center phonons, and with the Debye frequency measured in Ref.[1]. We conclude that although the experimental data for the specific heat jump and for the reduced gap are perfectly consistent with each other for each material separately (CaSiAl thus being in the strong, and SrSiAl in the weak coupling regime), they are radically inconsistent with the relatively small difference in T_c in the two materials.

Admittedly, we do not see a natural possibility to reconciles these data. A not-so-natural possibility is to as-

sume that the electron-phonon coupling in CaSiAl is enhanced by a soft mode, while in SrSiAl this mode is missing. Indeed, Carbotte's analysis does not applies to system with "unusual' structure of the Eliashberg function, $\alpha^2 F(\omega)$. In particular, soft modes of the order of $2\pi T_c$ (~35 cm^{-1}, for CaSiAl) may increase both $\delta C_p/\gamma T_c$ and $2\Delta/kT_c$ without raising T_c (see. e.g., Ref.[12]). Admittedly, it is hard to understand why such a mode would exist in one compound, but not in the other. One possibility is that the soft mode is associated with ordering (or, on the opposite, is eliminated by ordering). Another is that there is an inherent instability against formation of a superstructure (all calculated zone-center phonons are quite stable), and in fact CaSiAl is much closer to instability than SrSiAl. The third possibility is that the mode exists in both materials, but is insufficiently soft (compared to T_c) in SrSiAl to play an important role in superconductivity. It is also worth noting that short range ordering of some kind might be also increase the density of states of SrSiAl by further 10%, which would make the estimates of the electron-phonon coupling from the electronic specific heat coefficient and from the thermodynamics below T_c to agree with each other.
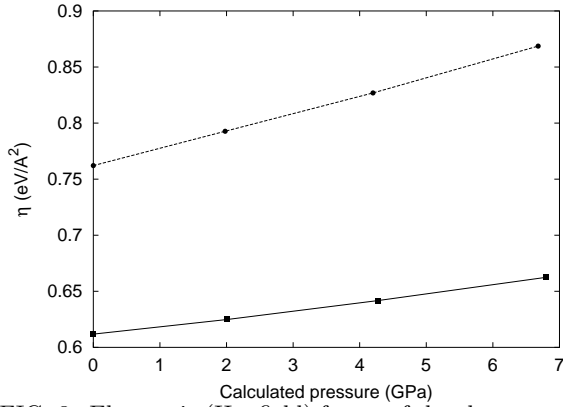

FIG. 3. Electronic (Hopfield) factor of the electron-phonon coupling constant in the rigid muffin tin approximation in the (in-plane) ordered structure. The full line corresponds to CaSiAl and the dashed one to SrSiAl.

Pressure effect. Finally, let us discuss the pressure effect on T_c discovered in Ref.[1], which appears to be substantial in both compounds, but positive in CaSiAl and negative in SrSiAl. The first consideration that comes to mind is that the pressure effect on the electronic structure is different. To verify that, we performed the rigid muffin-tin calculation as described above at three other volumes, corresponding to uniform linear compressions of 1, 2 and 3 %. The corresponding pressure we evaluated using the calculated LAPW-GGA equation of states, which gives the equilibrium lattice parameter with excellent accuracy (0.5% in SrSiAl and < 0.1% in CaSiAli; the calculated bulk moduli are 0.60 and 0.63 Mbar, respectively). While the rigid muffin-tin method strongly underestimates the coupling constant in the *sp* metals, it

should still be reliable in investigating structural trends. We found, however, that the calculated Hopfield factor *increases* in both compounds (note that the density of states, as usual, decreases with compression; the increase of η is due to increasing strength of the electron-ion scattering, predominantly on Ca/Sr). Therefor the observed disparity of the pressure dependence between the two compounds[1] must be due to lattice effects. An ultrasoft mode discussed above remains a valid possibility. According to Carbotte[11], a soft phonon mode is most efficient in raising T_c if its frequency is close to $2\pi T_c$, that is, around 35 cm^{-1} for CaSiAl. Therefore is a mode of such frequency is present in CaSiAl *and* in SrSiAl, hardening of such mode with pressure will depress T_c in the latter, but not in the former.

Conclusions To conclude, we report full-potential well converged calculations of the electronic structure and zone-center phonons in CaSiAl and SrSiAl, in order to gain better understanding of disparate superconducting properties of this otherwise very similar compounds. We also estimated the trends in electron-phonon coupling, using an approximate rigid-muffin tin method. We also assessed the stability of the disordered materials with respect to in-plane ordering and layered-type ordering, and found the considerable tendency to the former. Our results indicate that it is hardly possible to reconcile the superconducting properties of CaSiAl and SrSiAl using their electronic properties and conventional wisdom about the phonon-induced superconductivity. It may be possible to explain main experimental facts, assuming an ultrasoft mode of the order of 30-40 cm^{-1}, coupled with electrons. Whether this mode reflects a vicinity of a structural instability at some finite wave vector in an ordered crystal, or is somehow associated with short-range ordering is unclear. Experimental studies of ordering in CaSiAl and SrSiAl, and particularly connection (if any) between ordering and superconductivity is highly desirable, as well as low-energy lattice dynamics studies.

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TABLE I. Calculated frequencies of the zone-center phonons in the ordered structure, in cm^{-1}

	A_2''	A_2''	E'	E'
CaAlSi	100	212	187	456
SrAlSi	111	178	151	438

TABLE II. Electronic (Hopfield) factor of the electron-phonon coupling constant in the rigid muffin tin approximation, in $eV/Å^2$. "o" stands for the in-plane ordered structure, "v" for the virtual crystal approximation.

	Ca		Al		Si	
	o	v	o	v	o	v
CaSiAl	0.21	0.18	0.12	0.21	0.28	0.21
SrSiAl	0.33	0.27	0.14	0.22	0.29	0.22